UNCLASSIFIED

AD **406 120**

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

406 120

NOLTR 63-9

HEAT CAPACITY OF CRYSTALLINE
POLYMERS AT LOW TEMPERATURES

D D C

JUN 1? 1963

TISIA D

NOL

12 MARCH 1963

UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

HEAT CAPACITY OF CRYSTALLINE POLYMERS
AT LOW TEMPERATURES

Prepared by:
R. W. Warfield
M. C. Petree

ABSTRACT: Published heat capacity data on atactic and isotactic polypropylene, polyethylene and polytrifluoroethylene have been analyzed by the method of Starkweather. The results of this analysis indicate that the model proposed by Stockmayer and Hecht for the thermal motions of crystalline polymers at low temperatures can yield information indicative of the structure of the polymer.

PUBLISHED MAY 1963

APPROVED BY: F. ROBERT BARNET, Chief
                  Non-Metallic Materials Division

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

12 March 1963

HEAT CAPACITY OF CRYSTALLINE POLYMERS AT LOW TEMPERATURES

This report contains the results of an analysis of heat capacity data
on various crystalline polymers. The data have been analyzed by the
procedure of Starkweather to test the Stockmayer-Hecht model for the
heat capacity of a polymer. This study was carried out under Project
N10-a-1-56 as part of a general polymer investigation and is of importance
in furthering basic knowledge of polymer characteristics.

                                         R. E. ODENING
                                         Captain, USN
                                         Commander

                                         ALBERT LIGHTBODY
                                         By direction

CONTENTS

TABLES

ILLUSTRATIONS

REFERENCES

(a) Wunderlich, B., J. Chem. Phys., 37, 1203, 1207, (1962).
(b) Stockmayer, W. H., and Hecht, C. E., J. Chem. Phys., 21, 1954 (1953).
(c) Tarassov, V. V., J. Amer. Chem. Soc., 80, 5052 (1958).
(d) Warfield, R. W., and Petree, M. C., NATURE, 193, 1280 (1962).
(e) Warfield, R. W., and Brown, R., Kolloid Z.U.Z. Polymere, 185, 63 (1962).
(f) Warfield, R. W., and Petree, M.C., J. Polymer Sci., 55, 497 (1961); Makromol. Chem., 51 113 (1962).
(g) Isaacs, L. L., and Garland, C. W., J. Phys. Chem. Solids, 23, 311 (1962).
(h) Starkweather, H. W., J. Polymer Sci., 45, 525 (1960).
(i) Warfield, R. W., and Petree, M. C., Naval Ordnance Laboratory Technical Report 61-163 (1961).
(j) Dainton, F. S., Evans, D. M., Hoare, F. E., and Melia, T. P., POLYMER, 3, 277(1962).
(k) Sochava, I. V., Doklady Akad. Nauk., 130, 126 (1960).
(l) Dainton, F. S., Evans, D. M. Hoare, F. E., and Melia, T. P., POLYMER 3, 286(1962).
(m) Liang, C. Y., and Pearson, F. G., J. Mol. Spectroscopy, 5, 290 (1960).

INTRODUCTION

1. There has recently been a revival of interest in the heat capacities of crystalline and amorphous polymers. From heat capacity, C_V, data Wunderlich, (ref. (a)), has calculated the vibrational spectrum of a completely crystalline polyethylene (PE) and found that the models of Stockmayer and Hecht (ref. (b)), and of Tarassov (ref. (c)), are useful in understanding the thermal motions of linear polymers at low temperatures. We have also employed both Stockmayer-Hecht (refs. (d) and (e)), and Tarassov (ref. (f)) models in calculating the C_V of linear polymers at low temperatures and for calculating structural parameters. Recently Isaacs and Garland (ref. (g)), have measured the heat capacity of highly crystalline PE from 1.8° to 5.3°K and have interpreted their results in terms of the Stockmayer-Hecht model.

2. It is the purpose of this report to extend previous studies (refs. (d) and (e)), and to present the results obtained when the Stockmayer-Hecht model is applied to atactic (~16% crystalline) and isotactic (~40% crystalline) polypropylene (PPE) and to highly crystalline polyethylene and polytrifluoroethylene (PTriFE).

THE STOCKMAYER-HECHT THEORY OF HEAT CAPACITY

3. The model of Stockmayer and Hecht assumes that groups in the polymer chain vibrate as units and that there are strong primary bonds between the units and weak interactions between adjacent chains. Temperature dependence of heat capacity at low temperatures can then be expressed in terms of two ratios, $C_V/3Nk$ and T/T_M, where N is the number of vibrating units per gram; T_M (which is analogous to the Debye θ) equals $h\nu_m/k$, where h and k are the Planck and Boltzmann constants respectively, and ν_m is the maximum frequency of vibration. The analytical procedure of Starkweather (ref. (h)), was employed to evaluate the parameters, T_M, ν_m, and $3Nk$. Details of the calculations have been previously given (ref. (i)).

THE STARKWEATHER METHOD OF ANALYSIS

4. Starkweather (ref. (i)) has developed an analytical procedure for calculating the parameters T_M, ν_m, $3Nk$ and the molecular weight of the repeating unit. Briefly, the procedure is as follows: the experimental heat capacities are plotted logarithmically against the absolute temperature and this plot is placed over a similar logarithmic plot of $C_V/3Nk$ vs. T/T_M: the values of $C_V/3Nk$ and T/T_M being those given by Stockmayer and Hecht (ref. (b)). The upper (C_V vs. T) plot is shifted along the rectangular coordinates of the lower ($C_V/3Nk$ vs. T/T_M) plot until the curves superimpose. Then the experimental temperature corresponding to $T/T_M = 1$, is T_M and the Cp value corresponding to

$C_V/3Nk = 1$, is $3Nk$. It is assumed that at low temperatures $C_p - C_V$ is small. Composite plots of this type are shown in Figures 1, 2 and 3.

5. The experimental data for polyethylene are those recently obtained by Dainton and co-workers (ref. (j)), and the data for polytrifluoroethylene was obtained by Sochava (ref. (k)). Data for the atactic and isotactic polypropylene was obtained by Dainton and co-workers (ref. (l)). Values of the calculated parameters are given in Table 1.

DISCUSSION
6. The calculated value for ν_M of 529 cm^{-1} for PE is very close to the infrared band at 543 cm^{-1} while the calculated value of 226 cm^{-1} for PTriFE appears reasonable. In the case of atactic and isotactic PPE the calculated values of 325 cm^{-1} and 361 cm^{-1} appear to be associated with the bending motions of the main chain which, according to Liang and Pearson (ref. (m)), should appear near 400 cm^{-1}.

7. The calculated molecular weights of each of the vibrating units are in good agreement with the expected values, particularly in the case of PE. In the case of the two forms of PPE it would appear that the pendent -CH$_3$ group does rot make a large contribution to the heat capacity.

8. It is of interest to note that Isaacs and Garland (ref. (g)) considered the heat capacity of highly crystalline polyethylene in terms of the Stockmayer-Hecht model and were able to fit their experimental data and obtain a value of 885°K for T_M. This value can be compared with the value of 760°K given in Table 1.

9. Both Wunderlich (ref. (a)), and Isaacs and Garland (ref. (g)) have pointed out that the Stockmayer-Hecht model does not apply exactly to polyethylene (or to any other crystalline polymer). What is needed is a new and more exact model which takes into account the form of the crystal lattice of the polymer and the zig-zag chain structure. However, the degree of fit which has been obtained using the Stockmayer-Hecht model with simple linear polymers has been encouraging.

CONCLUSION
10. It can be concluded that the model of Stockmayer and Hecht is useful in understanding the thermal motions of crystalline polymers at low temperatures.

RECOMMENDATIONS
11. It is recommended that calorimetric measurements be made of heat capacity over a broad temperature range for a number of polymers. This data would be useful in testing the validity of the Stockmayer-Hecht model. Data of this type would also permit the calculation of the thermodynamic parameters, entropy, enthalpy, and free energy of the polymers considered.

TABLE 1

CALCULATED PARAMETERS FOR CRYSTALLINE POLYMERS

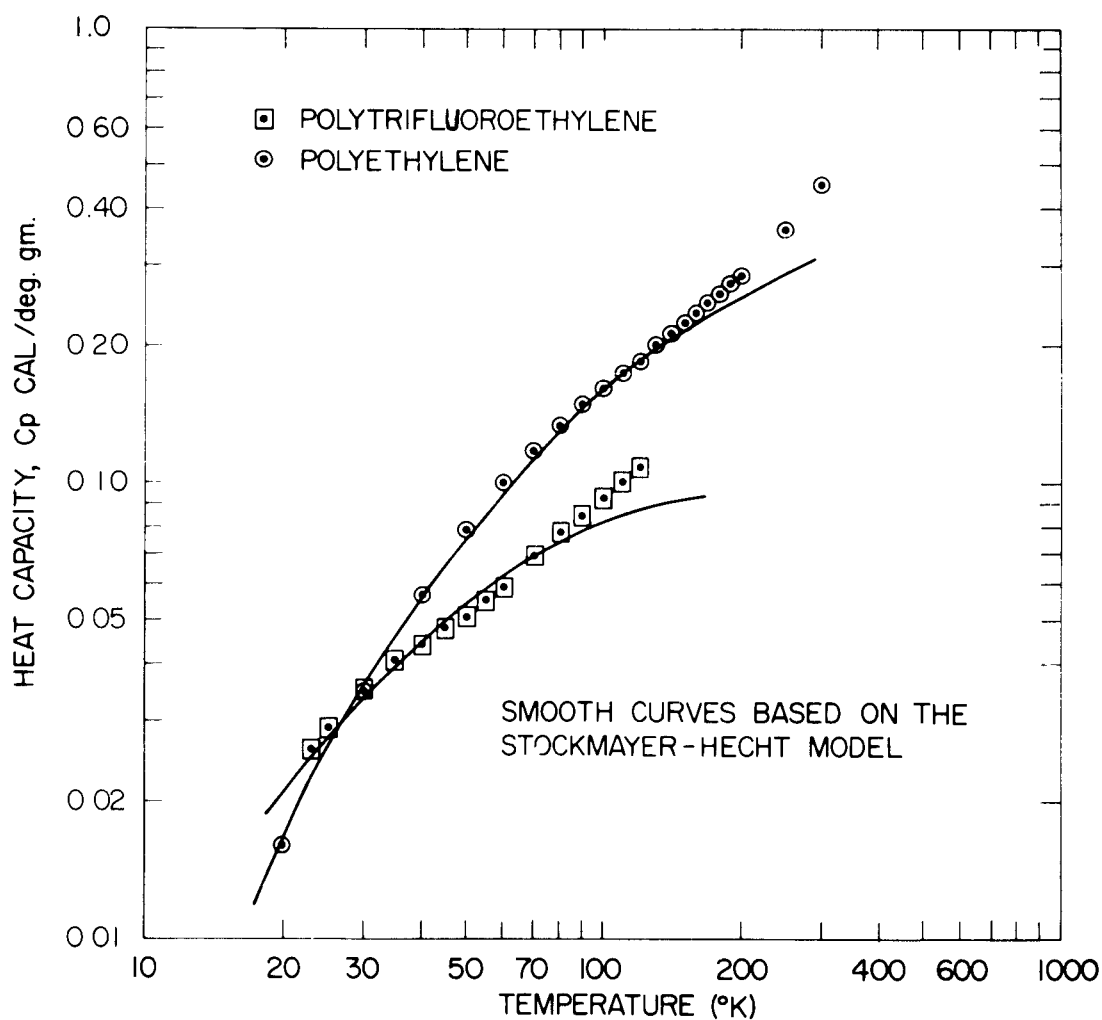| Parameter	Polyethylene	Polytrifluoro-ethylene	Atactic Polypropylene	Isotactic Polypropylene
Region of fit, °K	20-120°	23-70°	20-90°	20-95°
T_M, °K	760°K	325°K	466°K	519°K
$\sqrt{m}$, cm^{-1}	529	226	325	361
3Nk, CAL/ gm.deg.	0.348	0.104	0.242	0.238
Average Molecular Weight of Vibrating Unit, M(gm/mole)	17.1	57.3	24.6	25.2
Vibrating Units/ Repeating Units	0.82	1.43	1.71	1.67

FIG. I LOG-LOG PLOT OF HEAT CAPACITY VERSUS TEMPERATURE
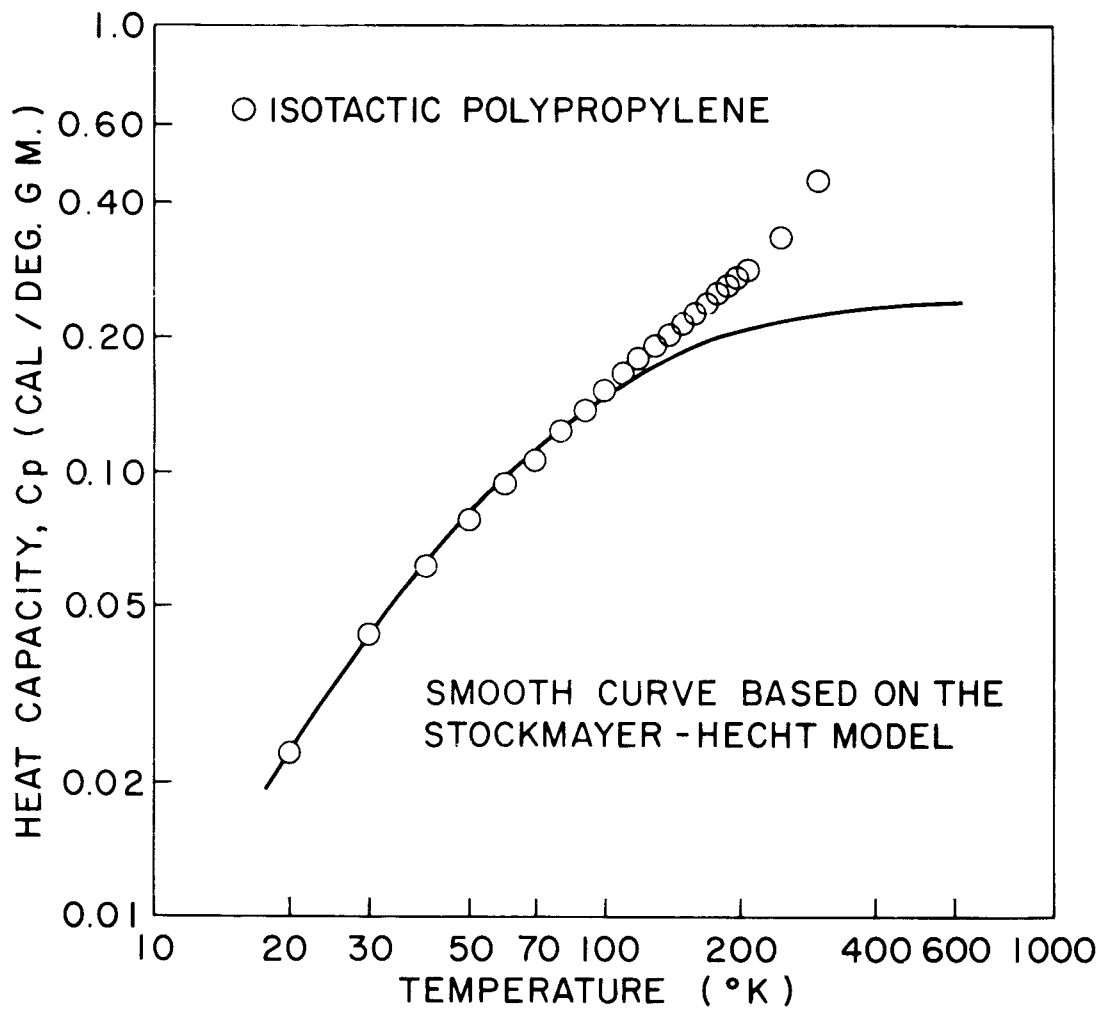
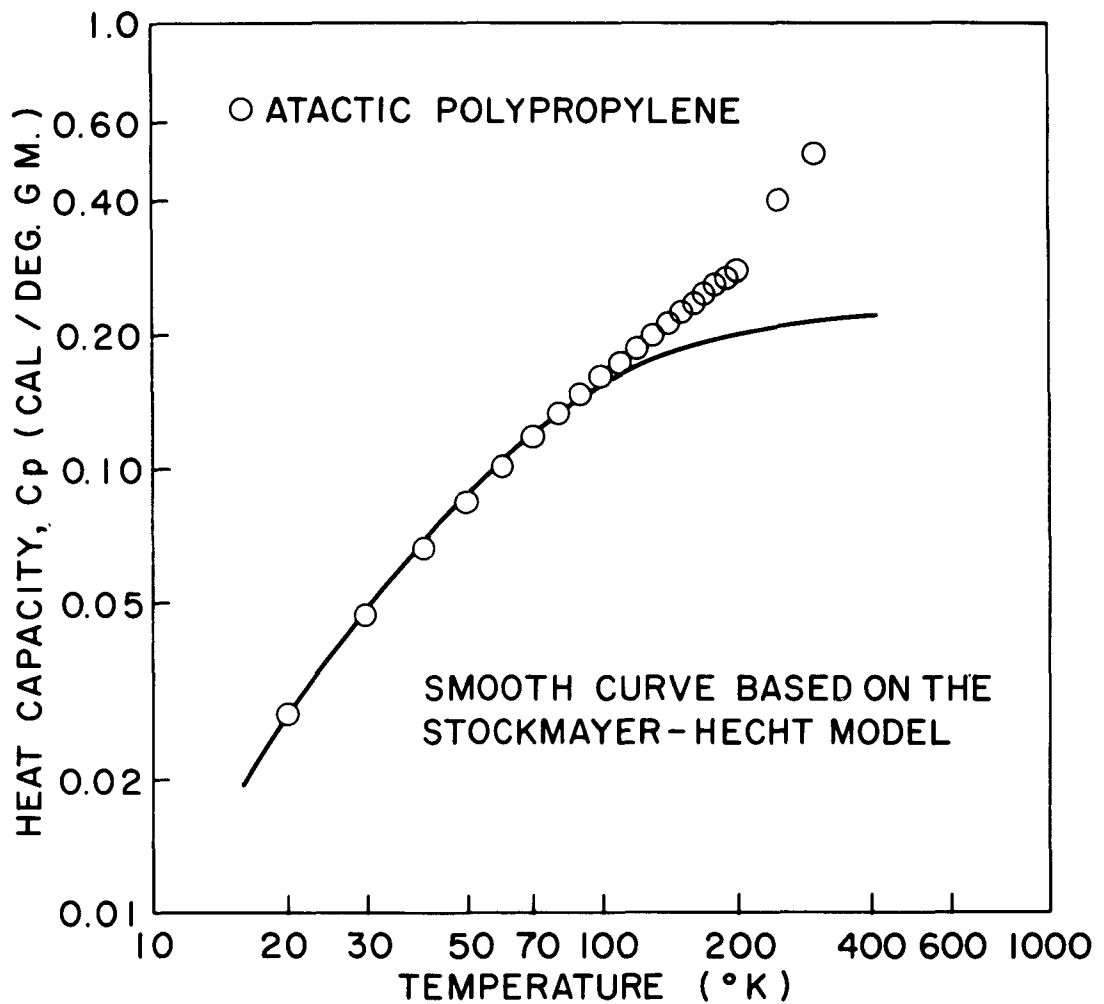FIG. 2 LOG-LOG PLOT OF HEAT CAPACITY VS TEMPERATURE FOR ISOTACTIC POLYPROPYLENE

FIG. 3   LOG-LOG PLOT OF HEAT CAPACITY
VS TEMPERATURE FOR ATACTIC
POLYPROPYLENE

DISTRIBUTION

Copies

Chief, Bureau of Naval Weapons
  RUSD-232 (H. Silk)
  RMMP-11 (I. Silver)
  RMMP-23 (S. J. Matesky
  RRMA (N. E. Promisell)
  RRMA-3 (P. Stone)
  RRMA-35 (J. Gurtowski)
  DIS-3 (Library)   4

Director, Special Projects Office
  SP2711 (H. Bernstein)

Chief, Bureau of Ships
  Code 346 (J. Alfers)
          (W. Graner)

Chief, Office of Naval Research
Navy Department
Washington 25, D. C.
  Attn: Code 423 (Dr. C. Klingsberg)

Director
Naval Research Laboratory
Washington 25, D. C.
  Attn: J. Kies

Commander
U. S. Naval Ordnance Test Station
China Lake, California

Commander
U. S Naval Ordnance Test Station
3203 E. Foothill Boulevard
Pasadena, California

Materials Laboratory
New York Naval Shipyard
Brooklyn 1, New York
  Attn: R. R. Winans

Commander
U. S. Naval Air Development Center
Johnsville, Pennsylvania

DISTRIBUTION

Copies

Air Force Systems Command
 Regional Office
C/O U. S. Navy Department
2305 Munitions Building
Washington 25, D. C.
  Attn: **Capt. H. Powell**

Commanding Officer
Air Force Ballistic Missile Division
Headquarters, Air Research and Development Command
 P. O. Box 262
Inglewood, California

Plastics Technical Evaluation Center
Picatinny Arsenal
Dover, New Jersey

Director
National Aeronautics and Space Administration
1512 H Street, N. W.
Washington 25, D. C.

Director
Forest Products Laboratory
Madison, Wisconsin

Director
Advanced Research Projects Agency
Department of Defense
The Pentagon
Washington 25, D. C.

Commander
Office of Scientific Research
Temporary Building D
Washington 25, D. C.

Armed Services Technical Information Agency   10
Arlington Hall Station
Arlington 12, Virginia
  Attn: TIPDR

CATALOGING INFORMATION FOR LIBRARY USE

BIBLIOGRAPHIC INFORMATION

	DESCRIPTORS	CODES	DESCRIPTORS	CODES
SOURCE	NOL technical report	NOLTR	Unclassified - 21	U421
REPORT NUMBER	63-9	63009		
REPORT DATE	12 March 1963	0263		

| | SECURITY CLASSIFICATION AND CODE COUNT |
| CIRCULATION LIMITATION |
| CIRCULATION LIMITATION OR BIBLIOGRAPHIC |
| BIBLIOGRAPHIC (SUPPL., VOL., ETC.) |

SUBJECT ANALYSIS OF REPORT

DESCRIPTORS	CODES	DESCRIPTORS	CODES	DESCRIPTORS	CODES
Heat	HEAT	Analysis	ANAL		
Capacity	CAPC	Stockmayer-Hecht	STHT		
Crystalline	CRYS	Measurement	MEAU		
Polymers	POLY	Model	MODE		
Low temperature	LOWM	Structure	STRC		
Polypropylene	PLYP	Polymers(Characteristics)	POLYC		
Polyethylene	POLH	Parameters	PARA		
Poly	POYA	Temperature	TEMP		
Tri	TRIY	Structure	STRC		
Fluoro	FUOR				
Ethylene	ETHY				
Starkweather	STWT				

PRNC-NOL-5970/28 (5-62)